

Modelling iron–clay interactions in deep geological disposal conditions

O. Bildstein *, L. Trotignon, M. Perronnet, M. Jullien

CEA DTN/SMT/MLMTE, CE Cadarache, 13108 St Paul lez Durance, France

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Abstract

In the context of deep geological disposal of high level radioactive wastes, the interactions between iron and clay-rich materials may lead to adverse transformations of clay minerals with a potential loss of confining properties such as swelling and capacity to exchange cations. Such transformations have been experimentally observed at temperatures starting at ca. 80 °C, where smectites contained in a mixture of bentonite and iron powder are transformed into iron-rich serpentine-type minerals.

The reaction-transport code CRUNCH is used to investigate the iron–clay interactions at 50 °C over a period of 10,000 years, which are the conditions considered here to represent the mean temperature value and the expected timescale for the corrosion stage. The aim is to predict the nature and quantity of corrosion product, calculate the chemistry of water (essentially the pH) and the mineralogical transformation in the system containing the canister, an optional engineered barrier (bentonite) and the host-rock (argillite).

The results of the calculations show that at the interface with the canister, where steel corrosion occurs, the iron is partly immobilized by the precipitation of iron oxides (essentially magnetite) and small amounts of siderite. The pH stabilizes at high values, between 10 and 11, at this location. In the bentonite or the argillite in contact with the container, the primary clay minerals are destabilized and iron-rich serpentine-like minerals precipitate as observed in the experiments (cronstedtite and berthierine). These minerals show low cation exchange and swelling capacities.

The results also show that the interactions between iron and clay may lead to significant porosity changes in the system. A reduction of the porosity is predicted at the surface of the steel canister, due to the precipitation of iron oxides. Porosity increase is predicted in the clay material due to the dissolution of the primary clay minerals. The effect of these porosity changes have yet to be observed experimentally and assessed with regard to the confinement capability of the repository near field, especially by considering the mechanical aspects in the case with and without the engineered barrier.

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1. Introduction

In deep geological nuclear waste disposal, stainless or carbon steel canisters will be put into physical contact with clay-rich materials from the host-rock and/or the engineered barrier systems (EBS) according to the common concepts in different countries (e.g., Andra, 2005). After the construction of the tunnels and the canister emplacement operations under ventilated conditions, the perturbed site will be unsaturated. After closure of the repository, the

region close to the waste packages, also called the near field (NF) system, will progressively resaturate and the corrosion of the canisters will start, releasing substantial amounts of iron in reduced conditions.

As a result of iron corrosion in the presence of clay, iron oxides, oxy-hydroxides and carbonates are forming (such as magnetite and siderite) as well as new Fe-rich phases growing in small tabular crystals in the Si–Al–Fe gels formed by the alteration of smectite and kaolinite. These final products are serpentine-like minerals such as berthierine, cronstedtite, and chamosite, described by Lantenois (2003), Papillon et al. (2003), Perronnet (2004), Jullien et al. (2005), and Lantenois et al. (2005), Perronnet et al.

* Corresponding author.

E-mail address: olivier.bildstein@cea.fr (O. Bildstein).

(in press). The alteration of clay minerals in the presence of steel, referred to as smectitic corrosion (Papillon et al., 2003), leads to adverse modifications in the cation exchange capacity (CEC), the swelling capacity, and possibly the mechanical and transport properties of the barriers (porosity/permeability increase). Indeed, the newly-formed Fe-rich phases take up less volume than the initial smectites and present a lower CEC: a decrease by a factor of 2 between the CEC of primary smectites and that of the secondary Fe-rich clay minerals was observed in batch experiments performed by Perronnet et al. (in press).

In addition, since magnetite and siderite are taking more volume in the pore space than the initial massive steel, a decrease of porosity is expected at the interface between the canister and clay. The effect of these porosity changes have to be further evaluated in combination with mechanical considerations, since porosity is also affected by the swelling of clays.

2. System description and model

The calculations of the evolution of the near field (NF) system are performed using a modified version of the reaction-transport model CRUNCH (Steeffel, 2001). The modifications include the possibility to maintain a strictly constant surface area for the corrosion of steel throughout the simulation, assuming that the generalized corrosion process affects the whole canister surface. Otherwise, the surface area would decrease according to the decrease of the steel volume fraction and the porosity, as it is classically modelled in reactive transport codes for all minerals in porous media. The NF system includes the steel container, the engineered barrier system (EBS) consisting of MX80 bentonite (a natural bentonite from Wyoming, USA) and the geological medium (Fig. 1), and is represented in a 1-D cartesian geometry.

2.1. Iron corrosion rate in clayey environments

The corrosion rate was measured in clays in various conditions and with various steel and clay materials. The value ranges between 0.1 and 20 $\mu\text{m}/\text{yr}$ for low cast iron, the pro-

cess having a mean activation energy of 11 kJ/mol (Smart et al., 2002; Foct and Gras, 2003; Papillon et al., 2003).

The corrosion process of steel is simulated by an irreversible dissolution of iron in the metallic form (Fe solid). A constant corrosion of 4.3 $\mu\text{m}/\text{yr}$ was considered in this paper for calculations at 50 °C (this value corresponds to a corrosion rate of 3 $\mu\text{m}/\text{yr}$ at 25 °C) (Foct and Gras, 2003). The potential corrosion products include iron oxides and hydroxides, iron carbonates, and iron-rich smectite and serpentine minerals as observed in experiments dedicated to steel corrosion in clayey environments (see Table 3).

2.2. System studied

The system is modelled using a 1-D purely diffusive domain, fully saturated with water, and open for diffusive exchange with water from the host-rock (Fig. 1). It comprises a 7 cm thick stainless steel canister, an 80 cm thick MX80-based EBS, and a 10 m long geological barrier of clay host-rock.

The porosity is updated according to the net volume balance of dissolved and precipitated minerals. The code is given a molecular diffusion coefficient at 25 °C for all the aqueous species ($D_0 = 10^{-9} \text{ m}^2/\text{s}$) and an activation energy for the diffusion process ($E_a = 13.8 \text{ kJ/mol}$) (Li and Gregory, 1974). The effective diffusion coefficient, D_{eff} , is calculated as a function of the porosity and updated during the simulation using Archie's law (Archie, 1942; see application to diffusion coefficients by Norton and Knapp, 1977; Skagius and Nieritnieks, 1986; Nakashima, 1995)

$$D_{\text{eff}} = D_0 \exp \left[-\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{298.15} \right) \right] \sigma^m$$

where σ is the porosity (–), m is the cementation factor (–), T is the temperature (K), and R is the gas constant (kJ/mol/K). The value of m is determined by fitting the effective diffusion coefficient measured at the Bure site (Andra, 2005): $\Phi = 15\%$ and $D_{\text{eff}} = 10^{-11} \text{ m}^2/\text{s}$ give $m = 2.5$, considering a temperature of 25 °C. This value is consistent with other studies on clayey materials (Nakashima, 1995; Manaka and Kawasaki, 2000; Van Loon et al., 2003).

Data for the equilibrium in the aqueous phase are taken from the EQ3/EQ6 database (Wolery, 1992). The kinetic parameters for mineral dissolution and precipitation are given in Table 3.

A major assumption with regard to clogging is that a volume clearance exists at the interface between the canister and the clayey material, referred to as the technological gap. This gap is necessary for the emplacement of the canister into the drift of the repository and is expected to be filled by the swelling bentonite upon rehydration. For the modelling, a 17 cm thick cell is considered which contains the steel canister, the technological gap and a fraction of clay (bentonite EBS or host-rock). The flux resulting from the interactions between iron and clay in the first cell diffuses into the clayey domain. The initial mineralogical

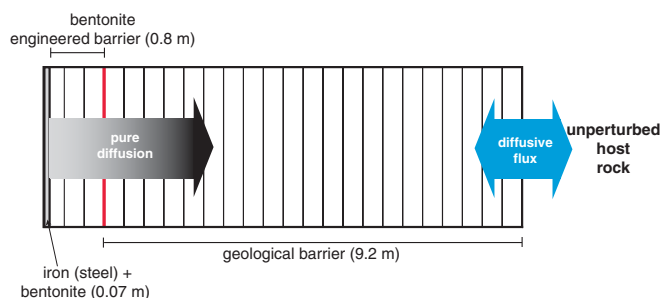


Fig. 1. 1-D domain for the iron–clay interaction calculations. The first cell is 17 cm thick and represents the canister cell containing iron but also the technological gap and a fraction of clay.

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